

PREPARATION AND LUMINESCENCE PROPERTIES OF SrWO₄ PHOSPHORS WITH Ce³⁺ DOPING

H. Y. FU^a, Y. K. GUO^a, Y. LI^b, Y. L. ZHUANG^a, H. T. FU^c, X. J. LI^a, L. G. JIN^{a,*}

^a*School of Materials Science and Engineering, Harbin University of Science and Technology, Harbin, China*

^b*Guangxi Key Laboratory of Optical and Electronic Materials and Devices, Guilin University of Technology, Guilin, China*

^c*School of Materials Science and Engineering, Chang'an University, Xi'an, China*

Efficient UV excitable Ce³⁺ ion activated SrWO₄ phosphors, which were successfully prepared through a hydrothermal method. X-ray diffraction, field-emission scanning electron microscopy, CIE color coordinates and photoluminescence were used to characterize the samples. The effect of adding pH solution on the luminescent properties of SrWO₄:Ce³⁺ was studied, the luminescence material SrWO₄:Ce³⁺ exhibits intense blue photoluminescence (PL) with the maximum peak located at 306 nm, which is ascribed to the 4f→5d transition of Ce³⁺, All these results indicate that the SrWO₄:Ce³⁺ phosphor holds tremendous potential for practical applications in and display with high performance LEDs.

(Received January 9, 2021; Accepted March 16, 2021)

Keywords: Hydrothermal, SrWO₄:Ce³⁺, Phosphor

1. Introduction

White light-emitting diodes (LEDs) have been widely used as solid-state lighting source owing to their excellent properties of lower power consumption, longer operation lifetimes, higher energy efficiency, and eco-friendly constituents. LEDs have superior advantages to the traditional incandescent and mercury-containing fluorescent lightings [1–4]. The current mainstream LEDs normally face the optical and thermal stable issues, For the purpose of overcoming the issues, rare earth doped tungstate to make luminescent materials has been proposed which have a scheelite type tetragonal structure with general formula AWO₄ (A = Sr, Ca, Ba) and their space group is I4₁/a. They have been studied widely due to their several applications in catalysts, scintillation detector, w-LEDs, photoluminescent devices, optics fiber, solar cell, fluorescent lamps and more [5-12], while inorganic hosts strontium tungstate (SrWO₄) have been well known for a long time for its strong visible luminescence in blue and green region at room temperature under UV excitation[13].

Despite the fact that the luminescence is mainly determined by the nature of the substituting ion, the host matrix into which this ion is embedded influences on the emission lines

* Corresponding author: 114668499@qq.com

intensity through its crystal field [14-17]. Lanthanide ions can emit light in the near UV, visible and infrared regions of the spectrum; each ion has a characteristic absorption and emission spectrum. Ce^{3+} has a strong spin and orbit coupling effect, which determines the pure color of light emitted by trivalent rare earth ions; therefore, materials activated by lanthanides are attractive for creating LEDs, fluorescent lamps, plasma displays, and active media for solid-state lasers[18-20]. However, in recent years, only laborious, poorly reproducible methods of producing nanoparticles are described in the literature for these objects. Hydrothermal methods are convenient for obtaining materials with different properties [21-25], compared with solid-phase methods; the recovery method differs in manufacturability, reproducibility, and the ability to produce a product [26-31].

In this work, $\text{SrWO}_4:\text{Ce}^{3+}$ nanocrystals were successfully synthesized by the hydrothermal method using highly pure $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Sr}(\text{NO}_3)_2$ and $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ powders as raw materials. We discussed the effect of crystallinity and morphology at different react time and different Ce^{3+} doping concentrations. Photoluminescent(PL) spectra and CIE chromaticity diagram of $\text{SrWO}_4:\text{Ce}^{3+}$ nanocrystals with at different solution PH were also investigated.

2. Experiment

2.1. Materials

Cerium nitrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) was purchased from Tianjin Guangfu Fine Chemistry Research Institute. Sodium tungstate ($\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$) was obtained from Tianjin Rui Jinte Chemical Co., Ltd. Strontium nitrate ($\text{Sr}(\text{NO}_3)_2$) was acquired from Tianjin Zhiyuan Chemical Reagent Co., Ltd. Anhydrous ethanol ($\text{C}_2\text{H}_5\text{OH}$) was provided by Tianjin Tianli Chemical Reagent Co. Ltd. All reagents were of analytical grade and used without any purification.

2.2. Hydrothermal synthesis of $\text{SrWO}_4:\text{Ce}^{3+}$

A series of $\text{SrWO}_4:\text{x}\%\text{Ce}^{3+}$ ($\text{x} = 1.0-7.0$) phosphors were synthesized by hydrothermal method. $\text{Sr}(\text{NO}_3)_2$ (6 mmol) and $\text{Ce}(\text{NO}_3)_3$ (6 mmol) was dissolved in deionized water (20 mL). Afterwards, 18 mL deionized water containing $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (6 mmol) was added and the resultant solution was stirred at room temperature for 30 min. The above mixing solution was transferred into a Teflon-lined stainless steel autoclave and sealed, maintained at 180 °C for 8-12 h. Finally, the precipitate was collected by centrifugation and washed several times with deionized water and ethanol, followed by oven-drying at 70 °C for 6 h. For the performance of $\text{SrWO}_4:\text{Ce}^{3+}$ phosphor in different pH environments, similar procedure was performed. Merely one more step was inserted. That is, after the addition of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, using HNO_3 and NaOH to adjust the pH to 3, 7 and 10.

2.3. Characterization

The SEM of samples were imaged using a JEM-2100 with a field emission gun operating at 120 kV. X-ray diffraction measurements were performed an X' Pert PRO MPD diffractometer using CuK α radiation ($\lambda=0.154$ nm). The PL were obtained from RF-5301PC fluorescence spectrophotometer produced by Shimadzu Corporation of Japan and using the light source of 150 W xenon lam.

3. Results and discussion

3.1. Structure and characterization

Fig. 1 displays the XRD patterns of SrWO_4 with different Ce^{3+} doping concentrations. The obtained diffraction peaks of all $\text{SrWO}_4:\text{Ce}^{3+}$ samples match well with the standard card of SrWO_4 (PDF No. 85-0587). None of the samples have any impurity phases, indicating that all the Ce^{3+} -doped SrWO_4 samples were of pure phase and Ce^{3+} ion was successfully incorporated into the SrWO_4 matrix and hardly affected its crystal structure. In summary, the sample belongs to tetragonal crystal. With the continuously increasing Ce^{3+} , the intensity of SrWO_4 diffraction peaks decreases, meaning that more Ce^{3+} filled in the tetragonal system which crystallinity of SrWO_4 is not excellent.

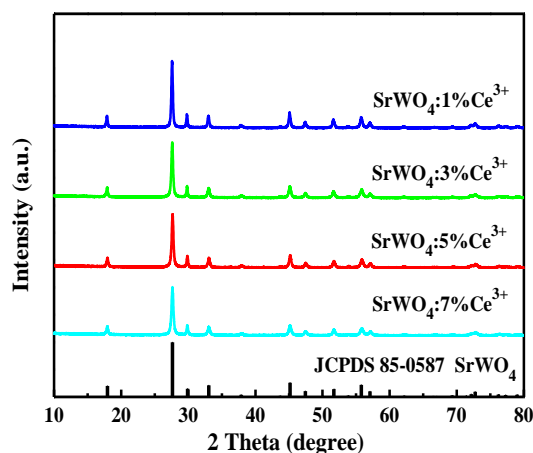


Fig. 1. X-ray diffraction patterns of $\text{SrWO}_4:\text{Ce}^{3+}$ samples.

$x = 3.0$, main crystalline phase of SrWO_4 with lower content of $\text{SrWO}_4:\text{Ce}^{3+}$ could be observed in the XRD pattern when the hydrothermal time is 8 h, as shown in Fig. 2. As the time increases up to 14 h, only stronger and sharper XRD peaks were observed indicating crystal perfection and growth.

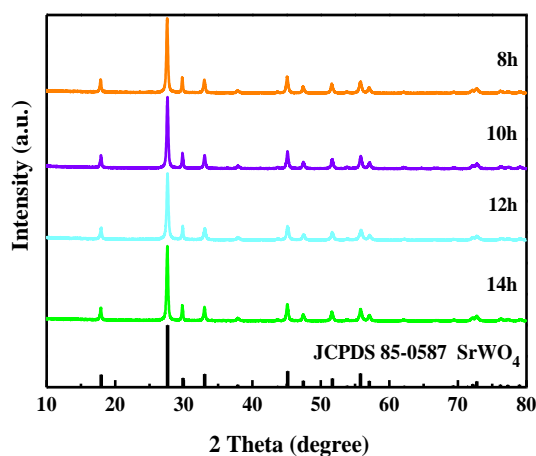


Fig. 2. X-ray diffraction patterns of reaction products synthesized at different time.

Fig. 3(a-d) displays the SEM images of the $\text{SrWO}_4 \cdot x\% \text{Ce}^{3+}$ ($x = 1, 3, 5$ and 7) phosphors prepared by simple hydrothermal method. The morphology of Fig. 3b obtained phosphor particles is relatively regular spherical and hamburger, which not only has a smooth surface, but also has an admirable dispersion. Fig. 3 (a, c, d) showed the shape of component particles of $\text{SrWO}_4 \cdot \text{Ce}^{3+}$ sample was discovered to be irregular; shape is more densely and has poor crystallinity.

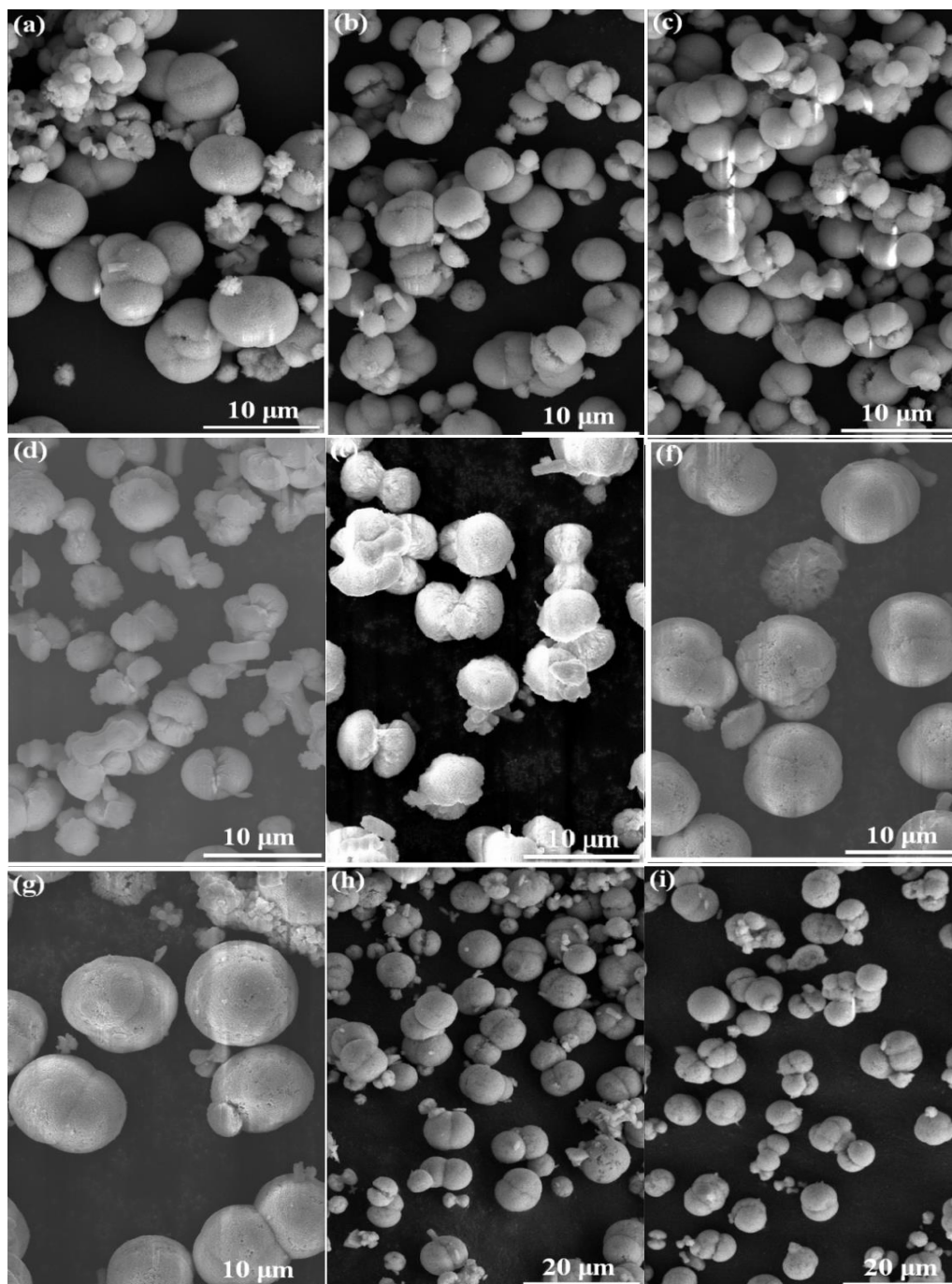


Fig. 3. SEM morphologies of $\text{SrWO}_4 \cdot \text{Ce}^{3+}$ with (a) 1 % Ce^{3+} , (b) 3 % Ce^{3+} , (c) 5 % Ce^{3+} and (d) 7 % Ce^{3+} reacted at $\text{pH} = 7$ for 12 h, 3 % Ce^{3+} reacted at $\text{pH} = 7$ for (e) 8 h, (f) 10 h and (g) 14 h, and 3 % Ce^{3+} reacted at (h) $\text{pH} = 3$ and (i) $\text{pH} = 7$ for 12 h.

The morphologies of $\text{SrWO}_4: 3\% \text{Ce}^{3+}$ phosphors at different time (8-14 h) were shown in Fig. 3 (e-g). It can be observed that the obtained of samples morphology was destroyed attributed to the long-term thermal stress when the time increased to 14 h or converted to stick and dumbbell when the time is too short (8-10 h) of sample has not been formed. Comprehensive morphology and XRD, $\text{SrWO}_4: 3\% \text{Ce}^{3+}$ phosphor synthesized by 12 h hydrothermal time were selected as the test sample material for the following experiments. Fig. 3 (h, i) shows the SEM micrographs of $\text{SrWO}_4: 3\% \text{Ce}^{3+}$ phosphors synthesized by 12 h under different pH. After the pH addition, morphology of Fig. 3 (h, i) without changed significantly compared to the $\text{SrWO}_4: 3\% \text{Ce}^{3+}$, that forming still spherical and hamburger structure, but the size has changed. The test results and experimental phenomena show that successful incorporation of pH has changed crystallinity and morphology of $\text{SrWO}_4: 3\% \text{Ce}^{3+}$. In summary, excessive acid or alkali environment will inhibit the growth of crystal grains, resulting in uneven particle size and large particle size gap.

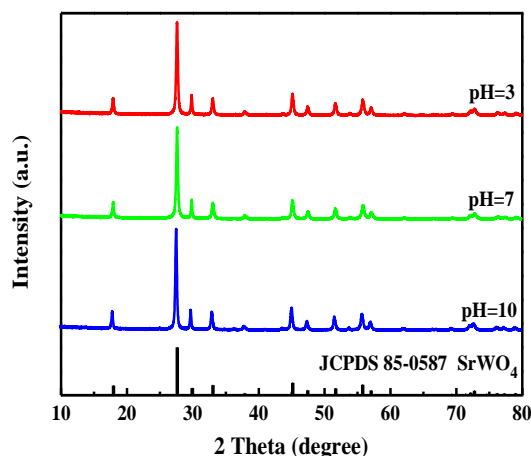


Fig. 4. XRD patterns of $\text{SrWO}_4: \text{Ce}^{3+}$ phosphor with different pH.

Fig. 4 shows the XRD patterns of the $\text{SrWO}_4: 3\% \text{Ce}^{3+}$ samples under different pH. The XRD patterns of phosphor added with pH solution matched well with that of SrWO_4 and hardly affected its crystal structure. These results indicate that our synthesized $\text{SrWO}_4: 3\% \text{Ce}^{3+}$ exhibit high crystallinity and purity after adding the pH, and gradually increase with increase of pH, the crystallinity of $\text{SrWO}_4: 3\% \text{Ce}^{3+}$ in Fig. 4i is better. Finally, combining SEM and XRD, we choose pH = 7 of the solution, hydrothermal time of 12 h and the molar ratio of Ce^{3+} is 3% to prepare $\text{SrWO}_4: \text{Ce}^{3+}$.

3.2. Photoluminescence properties

Fig. 5 illustrates the PL spectra of $\text{SrWO}_4: 3\% \text{Ce}^{3+}$ phosphors with different pH under 306 nm excitation. Clearly, the variation trends of emission intensities for $\text{SrWO}_4: 3\% \text{Ce}^{3+}$ with pH increasing concentration exhibited significant difference, but the position and shape of PL bands do not show appreciable change. The PL intensity of $\text{SrWO}_4: 3\% \text{Ce}^{3+}$ firstly increases and then decreases as the amount of pH solution doping increases, and reaches a maximum of 229.07 at a wavelength of 468 nm when the doping amount of pH is 7. It can be speculated that the non-radiative cross-relaxation among the adjacent activators, the neighboring Ce^{3+} ions pairs in $\text{SrWO}_4: 3\% \text{Ce}^{3+}$ phosphor, reduces the amount of the luminescence centers, thereby cutting down the luminous intensity.

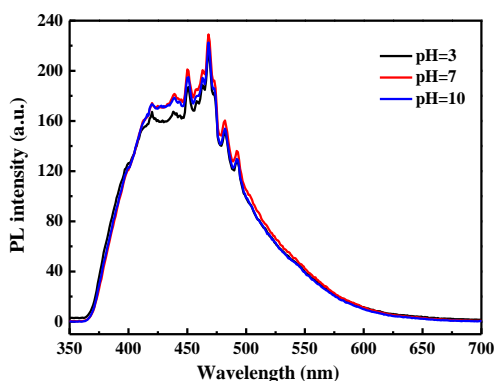


Fig. 5. The PL spectra of the $\text{SrWO}_4:3\% \text{Ce}^{3+}$ phosphors reacted for 12 h at different pH.

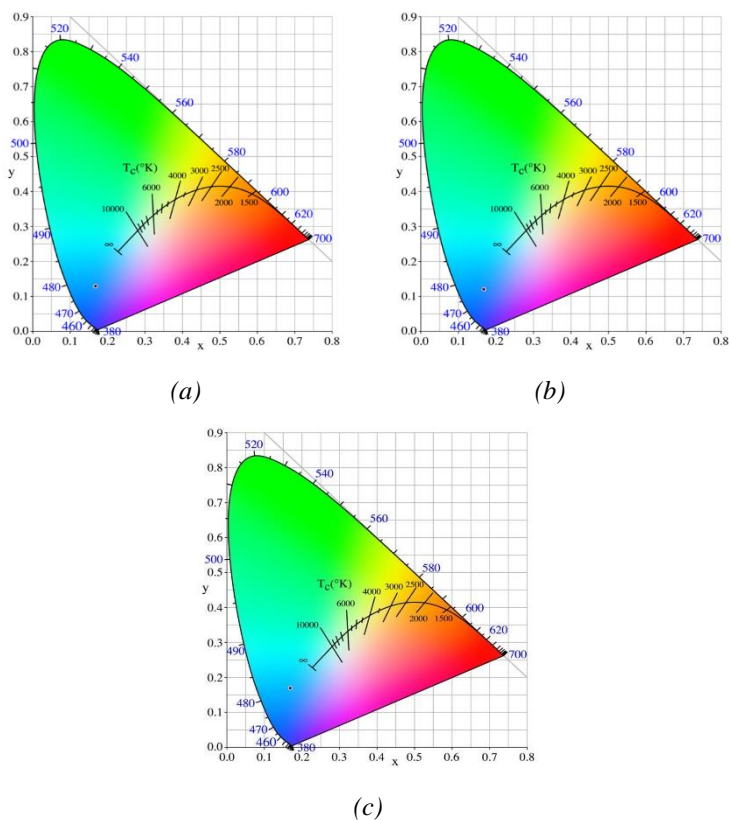


Fig. 6. CIE chromaticity diagram of $\text{SrWO}_4:3\% \text{Ce}^{3+}$ phosphors reacted for 12 h at different pH.

Fig. 6 shows the CIE chromaticity diagram of $\text{SrWO}_4:3\% \text{Ce}^{3+}$ samples under 306 nm excitation, it is found that the chromaticity coordinates of samples are located in the blue region. We found that the emission colors of these samples could be tuned by means of regulating the pH concentration in $\text{SrWO}_4:3\% \text{Ce}^{3+}$. Moreover, under the excitation of the UV lamp, the $\text{SrWO}_4:3\% \text{Ce}^{3+}$ phosphor of pH is 7 exhibited much brighter blue light than the pH is 3 and 10 counterpart, and has better saturation and chromogenicity. Therefore, when the pH of solution is 7, the fluorescence property of $\text{SrWO}_4:3\% \text{Ce}^{3+}$ is better.

4. Conclusions

In summary, the Ce³⁺ ions doped SrWO₄ phosphor was synthesized via hydrothermal method. Both XRD and SEM results indicate that these phosphors have better crystallinity and show uniform morphologies and particle size, meanwhile the optimum synthesis condition is using Ce(NO₃)₃·6H₂O, Sr(NO₃)₂ and Na₂WO₄·2H₂O as raw materials with an Ce³⁺ doping concentration of 3%, react for 12 hours at a solution pH of 7.

More importantly, under 306 nm excitation, the SrWO₄:Ce³⁺ phosphor presents a series of intense narrow-band blue luminescence peaks around 468 nm, indicating that the SrWO₄:Ce³⁺ has excellent application potential in the fields of display devices and light emitting diodes (LEDs).

Acknowledgments

This work was financially supported by the Open Foundation Guangxi Key Laboratory of Optical and Electronic Materials and Devices(20KF-14), China Postdoctoral Science Foundation (No. 2019M651940), and University Nursing Program for Young Scholars with Creative Talents in Heilongjiang Province (No. 2018204, No. 2018214).

References

- [1] S. Reineke, F. Lindner, G. Schwartz, N. Seidler, K. Walzer, B. Lussem, K. Leo, *Nature* **459**, 7244 (2009).
- [2] N. W. Rosemann, J. P. Eussner, A. Beyer, S. W. Koch, K. Volz, S. Dehnen, S. Chatterjee, *Science* **352**, 6291 (2016).
- [3] P. M. Pattison, J. Y. Tsao, G. C. Brainard, B. Bugbee, *Nature* **563**, 7732 (2018).
- [4] L. Zhang, B. H. Sun, C. Shao, F. Z. Zhen, S. Wei, W. Bu, Q. Yao, Z. G. Jiang, H. Chen, *Ceram. Int.* **44**, 14 (2018).
- [5] L. M. Dong, S. Wang, L. Chen, X. X. Jin, *Mater. Technol.* **34**, 2 (2019).
- [6] H. Q. Wang, M. Batentschuk, A. Osvet, L. Pinna, C. J. Brabec, *Adv. Mater.* **23**, 22 (2011).
- [7] L. M. Dong, J. T. Zhao, Q. Li, Z. D. Han, *J. Nanomater.* **2015**, (2015).
- [8] H. Dong, X. Zhang, Y. Lu, Y. Yang, Y. P. Zhang, H. L. Tang, F. M. Zhang, Z. D. Yang, X. J. Sun, Y. J. Feng, *Appl. Catal. B-Environ.* **276**, (2020).
- [9] E. Kifle, P. Loiko, C. Romero, J. R. V. de Aldana, A. Rodenas, V. Jambunathan, V. Zakharov, A. Veniaminov, A. Lucianetti, T. Mocek, M. Aguilo, F. Diaz, U. Griebner, V. Petrov, X. Mateos, *Opt. Express* **26**, 23 (2018).
- [10] F. M. Zhang, J. L. Sheng, Z. D. Yang, X. J. Sun, H. L. Tang, M. Lu, H. Dong, F. C. Shen, J. Liu, Y. Q. Lan, *Angew. Chem. Int. Edit.* **57**, 37 (2018).
- [11] L. L. Wang, Q. L. Wang, X. Y. Xu, J. Z. Li, L. B. Gao, W. K. Kang, J. S. Shi, J. Wang, *J. Mater. Chem. C* **1**, 48 (2013).
- [12] X. L. Liu, W. H. Hou, X. Y. Yang, J. Y. Liang, *Crystengcomm* **16**, 7 (2014).
- [13] P. Goel, R. Mittal, S. L. Chaplot, A. K. Tyagi, *Pramana-J. Phys.* **71**, 5 (2008).
- [14] J. B. Lian, F. Liu, J. Zhang, Y. Y. Yang, X. R. Wang, Z. R. Zhang, F. Liu, *Optik* **127**, 20 (2016).
- [15] X. Yang, Y. Z. Zhu, D. C. Ma, S. W. Long, Z. H. Liu, B. Wang, *Ceram. Int.* **45**, 8 (2019).
- [16] X. Li, J. B. Lian, *Optik* **127**, 1 (2016).

- [17] N. H. K. Nhan, T. H. Q. Minh, T. N. Nguyen, M. Voznak, *J. Ovonic Res.* **13**, 6 (2017).
- [18] X. B. Meng, J. L. Sheng, H. L. Tang, X. J. Sun, H. Dong, F. M. Zhang, *Appl. Catal. B-Environ.* **244**, (2019).
- [19] R. Shrivastava, J. Kaur, V. Dubey, *J. Fluoresc.* **26**, 1 (2016).
- [20] F. Yang, H. X. Ma, Y. F. Liu, B. Han, H. Feng, Q. M. Yu, *Ceram. Int.* **40**, 7 (2014).
- [21] H. Stark, R. L. N. Yatavelli, S. L. Thompson, H. Kang, J. E. Krechmer, J. R. Kimmel, B. B. Palm, W. W. Hu, P. L. Hayes, D. A. Day, P. Campuzano-Jost, M. R. Canagaratna, J. T. Jayne, D. R. Worsnop, J. L. Jimenez, *Environ. Sci. Technol.* **51**, 15 (2017).
- [22] Y. G. Denisenko, E. I. Salnikova, S. A. Basova, M. S. Molokeev, A. S. Krylov, A. S. Aleksandrovsky, A. S. Oreshonkov, V. V. Atuchin, S. S. Volkova, N. A. Khritokhin, O. V. Andreev, *Molecules* **25**, 6 (2020).
- [23] R. Luo, T. Li, Y. Chen, Z. L. Ning, Y. Zhao, M. J. Liu, X. Lai, C. Zhong, C. Wang, J. Bi, D. J. Gao, *Cryst. Growth Des.* **18**, 11 (2018).
- [24] M. Unni, A. M. Uhl, S. Savliwala, B. H. Savitzky, R. Dhavalikar, N. Garraud, D. P. Arnold, L. F. Kourkoutis, J. S. Andrew, C. Rinaldi, *Acs Nano* **11**, 2 (2017).
- [25] S. A. Osseni, Y. G. Denisenko, J. K. Fatombi, E. I. Sal'nikova, O. V. Andreev, *J. Nanostr. Chem.* **7**, 4 (2017).
- [26] P. O. Andreev, E. I. Sal'nikova, O. V. Andreev, Y. G. Denisenko, I. M. Kovenskii, *Inorg. Mater.* **53**, 2 (2017).
- [27] P. O. Andreev, E. I. Salnikova, I. M. Kovenskii, *Inorg. Mater.* **50**, 10 (2014).
- [28] O. V. Andreev, Y. G. Denisenko, E. I. Salnikova, N. A. Khritokhin, K. S. Zyryanova, *Russ. J. Inorg. Chem.* **61**, 3 (2016).
- [29] P. O. Andreev, E. I. Salnikova, O. V. Andreev, I. M. Kovenskii, *Russ. J. Phys. Chem. A* **90**, 1 (2016).
- [30] E. I. Salnikova, P. O. Andreev, S. M. Antonov, *Russ. J. Phys. Chem. A* **87**, 8 (2013).
- [31] P. O. Andreev, E. I. Salnikova, A. A. Kislitsyn, *Russ. J. Phys. Chem. A* **87**, 9(2013).